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By
R. K. Peterkop
(USSR)

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ON THE ASYMPTOTIC BEHAVIOR OF THE WAVE FUNCTION * OF A SYSTEM OF CHARGED PARTICLES

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R. K. PETERKOP

The asymptotic behavior of the wave function describing collision processes (e.g., ionization) that result in the formation of more than two free particles is well known, if all the particles that are formed are neutral and also if not more than two of them are charged (see, e.g., [1,2,3]). An asymptotic form for an arbitrary number of charged particles was proposed in [7], in which an asymptotic expansion containing powers of logarithms was obtained, similar to Fock's expansion [4,5,6]. The results of [7] were further developed in [8-11], as well as in [12,13]. The asymptotic form treated in these papers is subjected to criticism in [14]. However, the remarks made in [14] cannot be recognized as valid. A brief response to them is contained in [15]. In the present article the problem of the asymptotic behavior of the wave function is examined in greater detail. Greater attention is paid to those aspects of the problem which, because they were neglected, led to errors in [14].

^{*}An: Rasseyaniye Elektronov (Scatturiya Elutions or atoms).

na Atomakh, pp. 35 - 68

Riga, 1967.

1. System of Neutral Particles

In the case of short-range forces (it is sufficient if the interaction potential decreases faster than r^{-1}) the part of the wave function that describes the motion of N particles scattered after collision has an asymptotic behavior as $\rho \to \infty$:

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_1,\ldots,\mathbf{k}_N) e^{i\kappa\rho}, \qquad (1)$$

where

$$\varkappa = \sqrt{\frac{k_1^2}{m_1} + \ldots + \frac{k_N^2}{m_N}} = \sqrt{2E};$$
 (2)

$$\rho = \sqrt{m_1 r_1^2 + \ldots + m_N r_N^2}; \tag{3}$$

$$n = 3N - 1; \tag{4}$$

 \mathbf{r}_{i} is the radius vector; \mathbf{m}_{i} is the mass; \mathbf{k}_{i} is the wave vector (momentum) of the i-th particle (we are using a system of units in which h=1); $\underline{\mathbf{f}}$ is the scattering amplitude; and \mathbf{E} is the energy of the system.

In formula (1) the momenta and radius vectors are associated by the relation

$$\mathbf{k}_i = m_i \mathbf{z} \, \mathbf{p}^{-1} \, \mathbf{r}_i. \tag{5}$$

Expressing $\mathbf{k}_{\mathtt{i}}$ in terms of the velocity $\mathbf{v}_{\mathtt{i}}$, we get

$$\mathbf{v}_i = \kappa \, \rho^{-1} \, \mathbf{r}_i. \tag{6}$$

Relation (6) expresses the obvious fact that the equivalent of scattering cases in which N particles with velocities \mathbf{v}_{i} are formed is the asymptotic region of configuration space in which the radius vectors of the particles are proportional to these velocities. At the same time the separation between interacting particles should be so large that the motion of the particles can be considered free.

Obviously, relations (5), (6) correspond to the freemotion formula of classical mechanics

$$\mathbf{r}_{i} = \mathbf{v}_{i} \mathbf{t}, \tag{7}$$

where t is time.

Essentially, formula (1) states that when the interparticle separation is large, the particles move as free particles - the wave function is a superposition of plane waves. In order to get a clearer notion of the meaning of formula (1), let us consider the following superposition of plane waves:

$$\Phi (\mathbf{r}_{1}, \dots, \mathbf{r}_{N}) = g \int \delta \left(\frac{p_{1}^{2}}{m_{1}} + \dots + \frac{p_{N}^{2}}{m_{N}} - \varkappa^{2} \right) f(\mathbf{p}_{1}, \dots, \mathbf{p}_{N}) \exp (i\mathbf{p}_{1}\mathbf{r}_{1} + \dots + i\mathbf{p}_{N}\mathbf{r}_{N}) d\mathbf{p}_{1} \dots d\mathbf{p}_{N},$$
(8)

where

$$g = 2\varkappa \left(-2\pi i\varkappa\right)^{-\frac{n}{2}} \left(m_1 \dots m_N\right)^{-\frac{1}{2}}.$$
(9)

Generally speaking, any wave function can be expanded into a series (an integral) in plane waves, but a δ -type dependence on energy in the integrand may occur only in the case of free motion.

If $r_i \to \infty$, the major contribution to the integral (8) is made only by waves that correspond to the given region of configuration space. In other words, the integrand has stationary points defined by the conditions

$$p_i = \pm k_i, \tag{10}$$

where \mathbf{k}_{i} is determined according to (5). The minus sign in (10) refers to a wave moving toward the center (i.e., toward the converging wave). Using the stationary phase method and assuming that the amplitude of the converging wave in the asymptotic region being considered is zero, we find

$$\Phi \sim \Psi \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_1, \dots, \mathbf{k}_N) e^{i \times \rho}. \tag{11}$$

Thus, we can assume that Ψ represents superposition of plane waves at great distances.

Taking (5) into account, the index of the exponent on the right-hand sides of (1) and (11) is obtained as

$$i\kappa \rho = i \mathbf{k}_1 \mathbf{r}_1 + \ldots + i \mathbf{k}_N \mathbf{r}_N. \tag{12}$$

Formula (1) can be rewritten in the form

$$\Psi \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_1, ..., \mathbf{k}_N) \exp(i \mathbf{k}_1 \mathbf{r}_1 + ... + i \mathbf{k}_N \mathbf{r}_N).$$
 (13)

Thus, when separation is large, the superposition of plane waves reduce to a single wave. This fact has a completely clear meaning. Imagine a source of finite dimensions (a reaction zone) emitting particles. At short distances from the source particles emanating from various points in the reaction zone all pass through the same points in space. Consequently, at short distances there is no definite correlation between the direction of particle motion and the direction of the radius vector (it is never possible to disregard the fact that the source has finite dimensions). But as the distance increases, the number of cases in which the various directions intersect gradually disappears. At sufficiently great distances the reaction zone can be considered as a point particle source. The direction of particle motion in this case coincides with the direction of the radius vector, and this is expressed by formulas (5), (6).

Therefore, formula (1) has the following physical meaning.

- Particle motion can be considered free it is described by superposition of plane waves.
- 2. In this superposition all the components that do not correspond, in the sense of (5), (6), to the region of configuration space being considered vanish. Superposition of plane waves reduces to a single wave.

From this we get the conditions of applicability of formula (1).

- l. In the region of configuration space being examined the potential energy is negligibly small as compared to the kinetic energy.
- 2. The region being examined is so far from the reaction zone where interaction is actually taking place that the latter can be considered a point particle source.

With p as large as desired, the configuration space of many particles contains regions in which the interaction potential does not vanish. Even in this case, however, it can be assumed that collision actually takes place in a bounded zone. If the potential is repulsive, remote interaction regions quickly empty (with increasing distance), but if the potential is attractive, particles do not vanish. It goes without saying that formula (1) is not applicable in these regions.

2. System of Neutral and of Two Charged Particles

In cases when charged particles also form, the asymptotic behavior of the wave function has been known only for collision processes in which no more than two particles, in Coulomb interaction, are formed. Then the wave function at great distances is a superposition of functions in which the relative motion of both Coulomb particles is described by the well-known Coulomb

wave function, while the motion of their center of inertia and that of all the remaining particles is described by plane waves.

It is not difficult to obtain an asymptotic expression similar to (11) for the superposition of the products of plane waves and Coulomb functions.

A Coulomb function that has an "incident + convergent wave" asymptotic and is normalized analogous to a plane wave is

$$\varphi(\alpha, k, r) = \chi(\alpha, k, r) e^{ikr}, \qquad (14)$$

where $\chi(\alpha, k, r) = e^{-\frac{\pi\alpha}{2}} \Gamma(1 - i\alpha) F(i\alpha, l, -i(kr + kr));$ (15)

$$\alpha = \frac{Z\zeta}{V} ; \qquad (16)$$

and F is a degenerate hypergeometric function.

Function (14) satisfies the equation

$$\left(-\frac{1}{2m}\Delta + \frac{Z\zeta}{r} - \frac{mv^2}{2}\right)\varphi = 0. \tag{17}$$

Consider the asymptotic behavior of the following integral, different from (8) in that the plane waves are replaced by Coulomb functions:

$$\Phi_{K}(\mathbf{r}_{1},\ldots,\mathbf{r}_{N}) = g \int \delta\left(\frac{p_{1}^{2}}{m_{1}} + \ldots + \frac{p_{N}^{2}}{m_{N}} - \varkappa^{2}\right) f(\mathbf{p}_{1},\ldots,\mathbf{p}_{N}) \times \Phi(\alpha_{1},\mathbf{p}_{1},\mathbf{r}_{1}) \ldots \Phi(\alpha_{N},\mathbf{p}_{N},\mathbf{r}_{N}) d\mathbf{p}_{1} \ldots d\mathbf{p}_{N}.$$
(18)

only because the integrand contains the additional multipliers $\chi(\alpha_i,p_i,r_i)$. These additional functions oscillate considerably slower as $r_i \rightarrow \infty$ than do the exponents, and therefore their presence does not change the stationary point, which is determined by formula (10) in this case also. The multipliers $\chi(\alpha_i,p_i,r_i)$ at the stationary point can be considered as constants (everywhere equal to the value at this point) and together with the amplitude \underline{f} can be taken outside the integral sign. Considering further that if the vectors \underline{k} and \underline{r} coincide in direction, then as $r\rightarrow\infty$

$$\chi(\alpha, k, r) \sim \exp(-i\alpha \ln 2kr);$$
 (19)

we get finally

$$\Phi_{K} \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_{1}, \ldots, \mathbf{k}_{N}) \exp \left[i \left(\varkappa \rho - \alpha_{1} \ln 2k_{1} r_{1} - \ldots - \alpha_{N} \ln 2k_{N} r_{N} \right) \right]. \tag{20}$$

Here, as in the derivation of (11), the absence of a converging wave is assumed.

Formula (20) is obviously also applicable to the superposition of products of Coulomb functions and plane waves. Then, some $\alpha_1=0$. If all $\alpha_1=0$, then we get (11) from (20).

In the case when the integrand in (18) contains one Coulomb function and one plane wave, formula (20) corresponds to the results of [3], relating to the asymptotic behavior of the Green's function for a system consisting of one neutral and two charged particles.

Using (12) and (16), formula (20) can be rewritten in a form analogous to (13):

$$\Phi_{K} \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_{1}, \dots, \mathbf{k}_{N}) \exp \left[i \left(\mathbf{k}_{1} \mathbf{r}_{1} + \dots + \mathbf{k}_{N} \mathbf{r}_{N} - \frac{Z_{1} \zeta_{1}}{\nu_{1}} \ln 2k_{1} r_{1} - \dots - \frac{Z_{N} \zeta_{N}}{\nu_{N}} \ln 2k_{N} r_{N}\right)\right].$$
(21)

The conditions of applicability of formulas (20) and (21) are the same as for formulas (1),(11), and (13) (see p. 6). Formula (20) was derived in the same way as (11) except that additional use was made of (19). If the next term on the right-hand side of (19) is estimated using an asymptotic expansion of the degenerate hypergeometric function, we find that the applicability conditions (19) are

$$\frac{\alpha^2}{2kr} \ll 1; \qquad \frac{|\alpha|}{2kr} \ll 1. \tag{22}$$

This means that the Coulomb potential energy must be considerably less than the kinetic energy.

It is not difficult to see that the wave function can be represented in the form of (18) if the Coulomb potential energy of the system has the form

$$\sum_{i=1}^{N} \frac{Z_i \zeta_i}{r_i}.$$
 (23)

Note that, taking (6) into account,

$$\sum_{i=1}^{N} \frac{Z_i \zeta_i}{r_i} \sim \frac{\varkappa}{\rho} \sum_{i=1}^{N} \frac{Z_i \zeta_i}{v_i}$$
 (24)

as $\rho \rightarrow \infty$.

The number of charged particles is greater than two, the Coulomb potential energy of the system cannot be written in the form of (23), and the wave function of the system cannot be written in the form of a superposition of products of Coulomb functions and plane waves. Therefore (18) and (20) can have a direct physical meaning only if more than one of the α_i are different from zero. In this case the single Coulomb function describes the relative motion of both charged particles. Formulas (18) and (20) are applicable, e.g., to the problem of single ionization of a negative hydrogen ion by an electron, when a neutral atom and two electrons are formed. However, they are no longer applicable to the case of electron ionization of a hydrogen atom, when three charged particles are formed.

3. General Case of a System of Charged and Neutral Particles

An asymptotic form for the wave function of a system containing an arbitrary number of charged particles was proposed in [7]. Considered in this article was a system of N electrons in the field of a fixed nucleus. The Schrödinger equation can then be written in the form

$$\left[\frac{1}{\rho^{n}}\frac{\partial}{\partial\rho}\left(\rho^{n}\frac{\partial}{\partial\rho^{n}}\right) + \frac{\Delta^{*}}{\rho^{2}} - \frac{2V\left(\Omega\right)}{\rho} + 2E\right]\Psi\left(\rho,\Omega\right) = 0,\tag{25}$$

where $\Delta *$ is the angular portion of the Laplace operator in 3N-dimensional space; Ω is a collection of \underline{n} variables (angles) determining the directions in 3N-dimensional space. These variables determine the directions of the radius-vectors in three-dimensional space and the ratio of their absolute values. Taking (5) into account, it is clear that as $\rho \to \infty$, every Ω corresponds to a definite set of momenta $\mathbf{k_i}, \ldots, \mathbf{k_N}$. Thus, every direction Ω corresponds to a specific outcome of the collision. In the expression for the scattering amplitude the momenta can be replaced by Ω :

$$f(k_1, \dots, k_N) = f(\Omega).$$
 (26)

Note that the electron system being examined in the field of a fixed nucleus does not restrict the generality of the analysis. The Schrödinger equation for a system of N+1

charged particles with arbitrary masses and charges can also be reduced to the form of (25) using a center-of-inertia system.

It was demonstrated in [7] that equation (25) has a formal solution in the form of the series

$$\Psi(\rho, \Omega) = e^{-\frac{n}{2}} e^{i\kappa\rho - \frac{iV(\Omega)}{\kappa}\ln\rho} \sum_{m=0}^{\infty} \sum_{p=0}^{2m} A_{mp}(\Omega) \frac{(\ln \rho)^p}{\rho^m}.$$
 (27)

The specific form of the expansion follows uniquely from more general premises. The expansion coefficients A_{mp} are expressed in terms of various-order derivatives of $A_{oo}(\Omega)$ and $V(\Omega)$. For the existence of the expansion it is necessary that these two quantities be infinitely differentiable as functions of the angles in configuration space. Note that $A_{oo}(\Omega)$ is the scattering amplitude, while $V(\Omega)$ is equal to the product of ρ and the Coulomb potential energy of the system of particles.

Considering only the first term of expansion (27) and denoting $A_{oo}(\Omega) = f(\Omega)$, we have

$$\Psi(\rho, \Omega) \sim \rho^{-\frac{n}{2}} f(\Omega) e^{i\kappa\rho - \frac{i}{\kappa} V(\Omega) \ln \rho}. \tag{28}$$

The applicability conditions for formula (28) are the same as those for formula (1) (see p. 6). Let us remember that

one of the necessary conditions states that the potential energy must be considerably less than the total energy; that is,

$$\frac{|V(\Omega)|}{\mathfrak{o}} \ll E. \tag{29}$$

As is evident, (28) differs from (1) only in that the phase has a logarithmic term. Phase distortion due to scattering in a certain direction $\Omega_{\rm o}$ proves to be the same as for the solution of equation (25) with the potential independent of Ω (everywhere equal to $V(\Omega_{\rm o})\rho^{-1}$). It can be said that the asymptotic motion of a system of charged particles is the same as in the case when this system moves in configuration space with constant (direction-independent) Coulomb potential. This is a result to be expected. At great distances the motion of Coulomb particles approaches the motion of free particles asymptotically. The latter is characteristic in that the velocities do not change with time, while the ratio of distances tends to the ratio of velocities. Consequently, the components of Ω tend to constant limits. Hence it is clear that the function $V(\Omega)$ should also tend to a constant value.*

Expansion (27), analogous to the well-known Fock expansion [4-6], contains powers of logarithms.

^{*}It follows from (7) that $\Omega(t) \to \text{const} \equiv \Omega_0$ as $t \to \infty$, whence $V(\Omega(t)) \to \text{const} = V(\Omega_0)$.

Based on the example of the problem of electron ionization of a hydrogen atom at zero total orbital moment, it was also demonstrated in [7] that the phase we obtained for the wave function corresponds to the asymptotic behavior of the time-independent portion of the classical action

$$S(\rho, \Omega) \sim \kappa \rho - \frac{1}{\kappa} V(\Omega) \ln \rho.$$
 (30)

The validity of formula (30) for the general case was demonstrated in [8]. To derive (30) in [7,8], the first thing done was to determine the asymptotic behavior of the solutions to the equation of motion and then the action was computed as the integral along the trajectory. The problem of asymptotic behavior as considered within the framework of classical mechanics will be discussed in greater detail in the last section of this article.

The asymptotic form (28) was used in [9] to determine the asymptotics of a scattered wave and to establish relationships between the amplitudes of direct and exchange scattering during ionization. It was used in [10] to study the similarity of integral expressions for the amplitude. It was shown in [11], for the case of electron ionization of a hydrogen atom, that the logarithmic phase distortion we discovered also follows from the

• asymptotic behavior of an exact system of equations. Discussed in the same paper were other possible ways of writing the logarithmic term in the phase of the wave function; of these ways note

$$-\sum_{i>j} \frac{Z_i Z_j}{|\mathbf{v}_i - \mathbf{v}_j|} \ln |\mathbf{r}_i - \mathbf{r}_j|, \tag{31}$$

where Z_i and Z_j are the particle charges of the system being examined (including Z_o , which is the charge of a fixed center with zero velocity and radius vector).

That the logarithmic term is not unique is implied by the fact that any function of Ω can be added to it, simultaneously subtracting the same function from the phase of the scattering amplitude. Obviously, Ψ does not change in this case. The phase of the scattering amplitude is not specified in advance. Consequently, the logarithmic term is determined, in general, with accuracy up to an arbitrary function of the angles. Thus, for instance, $\ln \rho$ can be replaced by $\ln 2\varkappa_{\rho}$, which corresponds to the form which is used in writing the asymptotic of a single-particle Coulomb function. The non-uniqueness of the phase is also clear from the fact that any asymptotic expression that considers only infinitely increasing terms is determined, in general, with accuracy up to terms tending to finite limits.

According to (6), the Coulomb potential energy as $\rho \rightarrow \infty$ can be written in a form analogous to (24):

$$\sum_{i>j} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \equiv \frac{V(\Omega)}{\rho} \sim \frac{\varkappa}{\rho} \sum_{i>j} \frac{Z_i Z_j}{|\mathbf{v}_i - \mathbf{v}_j|}.$$
 (32)

Using (6) once again, we get

$$\frac{V(\Omega)}{\varkappa} \ln \rho \sim \sum_{i>j} \frac{Z_i Z_j}{|\mathbf{v}_i - \mathbf{v}_j|} \left(\ln |\mathbf{r}_i - \mathbf{r}_j| + \ln \varkappa - \ln |\mathbf{v}_i - \mathbf{v}_j| \right). \tag{33}$$

Hence it is evident that (31) is a possible expression for the logarithmic term in the phase.

Using (12) and (31), formula (28) can be rewritten in a form analogous to (13) and (21):

$$\Psi \sim \rho^{-\frac{n}{2}} f(\mathbf{k}_{1}, ..., \mathbf{k}_{N}) \exp \left[i \left(\mathbf{k}_{1} \mathbf{r}_{1} + ... + \mathbf{k}_{N} \mathbf{r}_{N} - \sum_{i>j} \frac{Z_{i}Z_{j}}{|\mathbf{v}_{i} - \mathbf{v}_{j}|} \ln |\mathbf{r}_{i} - \mathbf{r}_{j}|\right)\right].$$
(34)

The asymptotic form (28),(34) can be applied directly to the case of a system containing both charged and neutral particles [8,11]. Then expression (31) for the logarithmic term seems to be more natural, since it depends only on the charged particle coordinates. Transition to neutral particles is carried out by setting the corresponding charges equal to zero.

Obviously, if the Coulomb potential energy (32) is reduced to the form (23), then (34) changes into (21). Thus,

(34) is a generalization of (21). Taking (24) into account, it is not difficult to understand that (20) and (21) can also be written in form (28).

Let us clarify in what sense asymptotic form (28,34) can be represented as a superposition of the products of Coulomb functions describing the motion of individual particles in fields produced by some effective charges.

In order to construct such a superposition it is necessary to find effective charges ζ_i with which the Coulomb potential in the asymptotic region can be reduced to form (23):

$$\sum_{i>j} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \sim \sum_{i=1}^N \frac{Z_i \zeta_i}{r_i}.$$
 (35)

Using (24) and (32), we get

$$\sum_{i>j} \frac{Z_i Z_j}{|\mathbf{v}_i - \mathbf{v}_j|} = \sum_{i=1}^{N} \frac{Z_i \zeta_i}{v_i}.$$
 (36)

This condition ensures the equivalence of the logarithmic terms in the phase for (21) and (34).

In the general case the collection N of numbers ζ_i may satisfy (36) not for all, but only for some (no more than N) collections of values of \mathbf{v}_i , or, in other words, for several directions Ω . Thus, we can construct a superposition of the products of Coulomb functions of form (18) such that the same

asymptotic as the exact wave function holds in several ($\leq N$) given directions in configuration space. In all the other directions the asymptotics of these functions in the general case will be different.

If only one direction is given, then considerable arbitrariness prevails in the choice of the effective charges. For example, it can be assumed that all but one of them equal zero. The other possibility is that all ζ_i are identical.

A condition of form (36) must be taken into account in setting up integral expressions for the ionization amplitude [10].

A superposition of form (18) ensuring the correct asymptotic in all directions can be constructed if the effective charges are assumed to be not constant, but dependent on the momenta $\mathbf{p}_1, \ldots, \mathbf{p}_N$ in accordance with the condition

$$\sum_{i=1}^{N} \alpha_{i} \equiv \sum_{i=1}^{N} \frac{Z_{i} \zeta_{i}}{p_{i}/m_{i}} = \sum_{i>j} \frac{Z_{i} Z_{j}}{|p_{i}/m_{i} - p_{j}/m_{j}|}.$$
 (37)

In this case the above-mentioned arbitrariness in the choice of $\zeta_{\dot{1}}(\text{or }\alpha_{\dot{1}})$ also prevails.

The result of the presence of the logarithmic term in the phase is that the usual methods of expansion in a system of functions of the angles are not applicable to $\,\Psi$. In the

asymptotic form of the wave function not only the scattering amplitude is dependent on the angles, as in the case of shortrange forces, but also the logarithmic term in the phase. Therefore, expansion of the wave function into a series with respect to a system of functions of angles will not, generally speaking, correspond to expansion of the scattering amplitude into a series in the same functions. Radial functions will not correspond to partial amplitudes. In order for this to occur, the multiplier with the logarithmic phase would first have to be isolated from the wave function before expansion. This factor may complicate numerical computations to a considerable extent. An exception is the case when $V(\Omega)$ depends additively on the arguments of the different angle functions. Another exception is the case when the expansion is carried out with respect to functions having an asymptotic analogous to plane waves, i.e., functions describing motion in a specific direction (infinity), so that $V(\Omega)$ has a definite value at infinity. In the latter case expansion in the asymptotic region is analogous in form to superposition (18), with the condition that α_i be determined in accordance with (37). Thus, for example, in the problem of electron ionization of a hydrogen atom, the expansion

$$\Psi = \int F_{\mathbf{k}}(\mathbf{r_1}) \, \psi_{\mathbf{k}}(\mathbf{r_2}) \, d\mathbf{k} \tag{38}$$

is admissible for the continuous-spectrum part on the basis of this viewpoint, but

$$\Psi = \sum_{lm} \int_{0}^{\infty} F_{klm}(\mathbf{r}_1) \, \psi_{klm}(\mathbf{r}_2) \, dk \tag{39}$$

is inapplicable.

The integral expressions for amplitude obtained in . [10] were used in [12] to derive a threshold law for the ionization cross section. It was found that the cross section near threshold depends linearly on the energy. This result was obtained by going to the limit E=0 in the integrand. When this is done, however, the integrand converges only by means of an additional exponential multiplier. Therefore, a further analysis of this problem is desirable.

The asymptotic behavior of the wave function was considered by a somewhat different method in [12,13] for the problem of electron ionization of a hydrogen atom. In a way similar to that of Bohm [18], the desired solution was represented in the form

$$\Psi(\rho,\Omega) = G(\rho,\Omega) e^{iU(\rho,\Omega)},$$
 (40)

where G and U are real.

By means of successive approximations it was shown that when $\ \mbox{\scriptsize o} \rightarrow \infty$

$$U \sim S \sim \kappa \rho - \frac{1}{\kappa} V(\Omega) \ln 2\kappa \rho;$$
 (41)

$$G \sim \rho^{-\frac{5}{2}} f(\Omega),$$
 (42)

. where S is the action (the solution of the Hamilton-Jacobi equation).

Expression (41) is equivalent to (30), since it differs by a term independent of ρ . In contrast with [7,8], the asymptotic behavior of the action was determined in [12,13] by solving the Hamilton-Jacobi equation by successive approximation.

The asymptotic form for E=0 was also proposed in [12,13], which was not done in [7,11]. When E=0, the Hamilton-Jacobi equation has a solution of the form

$$S(\rho,\Omega) = a(\Omega) \sqrt{\rho}. \tag{43}$$

Instead of (42), when E = 0, we have

$$G \sim \rho - \frac{9}{4} b(\Omega)$$
 (44)

In contrast with (42), where \underline{f} can be chosen arbitrarily (it is determined if all the boundary conditions of the scattering problem are taken into account), \underline{b} as a function of Ω should

satisfy a specific partial differential equation. It remains unclear to what extent this equation is compatible with the possible boundary conditions.

By somewhat supplementing the results of [12,13] we note that when E=0 we can construct a formal solution to equation (25) in the form of the series

$$\Psi(\rho, \Omega) = \rho^{-\frac{n}{2} + \frac{1}{4}} e^{ia(\Omega)^{1/\rho}} \sum_{m=0}^{\infty} b_m(\Omega) \rho^{-\frac{m}{2}}$$
(45)

In doing so, however, $b_o(\Omega)$ must satisfy the above-mentioned partial differential equation (in expansion (27), $b_o(\Omega)$ can be chosen arbitrarily) in order to exclude positive powers of expansion. Note that there are no logarithmic terms in (45), and the expansion is carried out in powers of $\sqrt{\rho}$.

Reference [13] also contains an extensive review of the various aspects of asymptotic behavior, considered on the basis of the problem of electron ionization of a hydrogen atom.

Recently there appeared an article by Temkin [14] in which the asymptotic form considered in [7-13] is taken to be incorrect. Let us briefly note the basic critical remarks made in [14].

- l. The logarithmic term in the phase of the asymptotic form (28) is singular at the points where the potential energy has a singularity, e.g., at $\mathbf{r_i} = \mathbf{r_2}$. At such points asymptotic form (28) does not satisfy the requirements for the behavior of the wave function as defined by the theorems of Kato.
- 2. It is not true that the Schrödinger equation reduces to an ordinary differential equation with respect to ρ as $\rho \rightarrow \infty$; that is, that the term containing Δ^* can be neglected in (25). For partial solutions, even when $\rho \rightarrow \infty$, terms containing derivatives with respect to the angles Ω should be given due regard. In the case of short-range forces such terms vanish for the asymptotic form of the superposition of partial solutions. But it should be expected that this will not be true in the case of Coulomb interaction.
- 3. If the derivative of the potential in some direction in configuration space has a discontinuity, then by differentiating (28) we find that the corresponding derivative of the wave function also undergoes a discontinuity, which is not permissible.
- 4. Using a simple model as an example, it can be demonstrated that there exists another asymptotic form which does not have the above-mentioned deficiencies.

Presented below are some brief responses to these remarks. A more detailed analysis will be given in later sections of this article.

- 1) Asymptotic form (28) corresponds to free motion. It is senseless to apply it in a region where the potential energy is greater than the total energy of the system.
- 2) The existence of a formal solution in the form of series (27) indicates that the asymptotic form is self-consistent. By differentiating (28), we can see that the terms containing angular derivatives have an additional multiplier $\rho^{-2}(\ln \rho)^{j}(j=1,2)$. Thus, the part of the Hamiltonian that contains Δ^* , analogous to the case of short-range forces, makes no contribution in the first term of the asymptotic expansion of the superposition of partial solutions. This also agrees with the asymptotic behavior of the Hamiltonian function in classical mechanics.
- 3) If the derivative of the potential has a discontinuity, then the derivative of the asymptotic form is not equal to the asymptotic form of the derivative of the wave function, that is, the asymptotic form cannot be differentiated. This can be demonstrated using as example the solution to the Hamilton-Jacobi equation of classical mechanics.
- 4) The suggested "second asymptotic form" corresponds to the superposition of the products of plane waves and Coulomb functions of type (18). But according to (20) this is equivalent to the asymptotic form that is being criticized. The author of [14] denies that the stationary phase method is applicable to the

example he is considering, in view of the fact that this method leads to a result in which the derivative of the wave function undergoes a discontinuity. But, as has already been mentioned in the preceding part, the discontinuity stems from illegal differentiation.

It should be noted that the example considered in [14], the so-called zero—order problem, corresponds to the case of one neutral and two charged particles. Therefore, the criticism of [14] refers not only to the results of [7-13], but primarily to the results of an earlier article [3].

4. Model of One-Dimensional Particles

The critical remarks of [14] were extensively due to the fact that certain features of asymptotic behavior that are characteristic not only of Coulomb forces, but also of short-range forces, were disregarded. At the same time, the fact that the space is three-dimensional is not essential. For greater clarity, therefore, let us consider a model analogous to the collision of electrons with hydrogen atoms, but assuming that the particles are one-dimensional and the interparticle forces are short-range. The wave-function properties of several particles, based on a similar model, were discussed in [16]. Using the same model as an example, the problem of flux conservation during collision was examined in [17].

Let x_1 and x_2 denote the coordinates of the first and second electrons (they will be taken to be different). The configuration space of the two electrons is a plane (Figure 1).

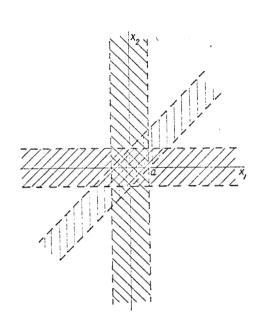


Figure 1. Plane of configuration of the two one-dimensional particles.

The Schrödinger equation has the form

$$\left[-\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} + U(x_1) + U(x_2) + U_{12}(x_1 - x_2) - E \right] \Psi(x_1, x_2) = 0, \tag{46}$$

where U is the attraction potential (e.g., a well), and U₁₂ is the repulsion potential (e.g., a barrier). In Figure 1 the shaded areas are those in which the potentials are non-zero. The potentials are chosen with the same interaction radii:

$$U(x) = U_{12}(x) = 0$$
, if $|x| > a$. (47)

At distances from the center greater than 2a, the configuration space is divided into four different regions. In three of them one of the potentials U or U_{12} is different from zero. In the fourth all the potentials equal zero.

Consider the region where only $U(x_2)\neq 0$ (that is, $|x_1|>2a$, $|x_2|< a$). The partial solutions to equation (46) in this region are

$$\Phi_{n}(x_{1}, x_{2}) = \psi_{n}(x_{2}).e^{ik}ln^{x}l,$$
 (48)

where ψ_n satisfies the equation

$$\left[-\frac{1}{2}\frac{d^{2}}{dx_{2}^{2}}+U(x_{2})-\epsilon_{n}\right]\psi_{n}(x_{2})=0, \tag{49}$$

while k_{ln} and ε_{n} satisfy the energy conservation condition

$$\frac{k_{\ln}^2}{2} + \epsilon_n = E. \tag{50}$$

The overall solution is obtained by summing all possible partial solutions. At the same time the constraints imposed by the boundary conditions must be taken into account. Let us suppose that electron 2 in the atom is found to be in the state ψ_0 before collision, while electron 1 is incident with the momentum k_0 . All other terms of the sum must contain only waves emanating from the center. Isolating the incident wave, we write

$$\Psi_{1} = \psi_{0}(x_{2}) \left[e^{ik_{0}x_{1}} + \sum_{n} f(k_{1n}) \psi_{n}(x_{2}) e^{ik_{1}nx_{1}} + \int f(k_{1}, k_{2}) \psi_{k_{2}}(x_{2}) e^{ik_{1}x_{1}} k_{1}^{-1} dk_{2}, \right]$$
(51)

where in the continuous-spectrum part

$$\frac{k_1^2}{2} + \frac{k_2^2}{2} = E. ag{52}$$

The function $e^{ik_2} x_1$, if $k_1 > 0$, describes motion in the positive direction of the axis x_1 , but if $k_1 < 0$, it describes it in the negative direction. Therefore, according to the boundary conditions, k_{ln} and k_{l} in (51) are positive in the region $x_1 > 0$ and negative in the region where $x_1 < 0$. The amplitudes f, of course, depend on the sign of the momentum. Thus, (51) represents two different functions. One of them is a solution for $x_1 > 2a$, and the other when $x_1 < -2a$.

In the region where only $\mathrm{U}(\mathrm{x}_1)$ is different from zero, there is no incident wave, and then we get

$$\Psi_{2} = \sum_{n} g(k_{2n}) \psi_{n}(x_{1}) e^{ik_{2n}x_{2}} + \int g(k_{2}, k_{1}) \psi_{k_{1}}(x_{1}) e^{ik_{2}x_{2}} k_{2}^{-1} dk_{1}.$$
 (53)

Here, analogously, the momenta k_{2n} and k_{2} are positive for positive x_{2} and negative for negative x_{2} .

In the region where only the electron interaction potential is different from zero, the following are partial solutions:

$$\Phi_k(x_1, x_2) = \varphi_k(x_{12}) e^{iKX}, \tag{54}$$

$$X = \frac{1}{2} (x_1 + x_2); \ x_{12} = x_1 - x_2;$$

$$\frac{1}{4} K^2 + k^2 = E. \tag{56}$$

Solution (54) describes the relative motion of the two electrons (with momentum $\,k\,$ and mass 1/2) and the free motion of their center of inertia (with momentum $\,K\,$ and mass 2). In this case bound states are absent and the wave function has the form

$$\Psi_{s} = \int h(k, K) \varphi_{k}(x_{12}) e^{iKX} K^{-1} dk.$$
 (57)

In conformity with the boundary conditions, K and X must have the same sign.

Finally, in the region where all the potentials are zero, the solution is equal to the superposition of plane waves:

$$\Psi_{4}^{*} = \int g(\kappa_{1}, \kappa_{2}) e^{ik_{1}\kappa_{1}} e^{ik_{2}\kappa_{2}} k_{2}^{-1} dk_{1}, \tag{58}$$

where k_1 and k_2 satisfy (52) and have the same signs as x_1 and x_2 .

We introduce the coordinates

$$\rho = \sqrt{x_1^2 + x_2^2}; \quad \alpha = \operatorname{arctg} \frac{x_2}{x_1} \tag{59}$$

and examine the asymptotic behavior of the wave function when $\,\alpha\,$ is fixed while $\,\rho\,\rightarrow\,\infty$.

The directions $\alpha=0$, $\frac{\pi}{4}$, $\frac{\pi}{2}$, π , $\frac{5\pi}{4}$, and $\frac{3\pi}{2}$ are said to be singular. As is evident in Figure 1, the potential does not vanish in these directions even at great distances. The behavior of the wave function in these directions is determined by formulas (51), (53), (57).

If α is not equal to any one of the singular quantities, then for a sufficiently large ρ it is impossible to avoid getting in the region where all the potentials are zero. Thus, for all α except the singular directions the wave function with ρ sufficiently large is a superposition of plane waves (58). It is not difficult to comprehend that the closer α is to a singular value, the greater ρ must be in order to escape from the effective range of the potential. In other words, if α tends to a singular value, the domain of application of formula (58) recedes to infinity. This inescapable fact is treated in [14] as a defect of the asymptotic form which ostensibly can and should be eliminated.

At large x_1 and x_2 the fundamental contribution to integral (58) is made by the neighborhood of the point defined by the conditions

$$k_1 = \kappa \rho^{-1} x_1; \ k_2 = \kappa \rho^{-1} x_2 \ (\kappa = \sqrt[1]{2E})$$
 (60)

$$k_1 = \varkappa \cos \alpha; \ k_2 = \varkappa \sin \alpha. \tag{61}$$

In a manner analogous to (11) the stationary phase method is used to find

$$\Psi_4 \sim q \ (k_1, k_2) \sqrt{\frac{2\pi}{i \varkappa \rho}} e^{i \varkappa \rho}.$$
 (62)

It is clear that ψ_n (x_2) satisfies (49) at all values of x_2 ; that is, even at those for which $U(x_2) = 0$. Consequently, ψ_1 is a solution also in the region where the potential is absent. This is also true of the functions ψ_2 and ψ_3 . Let us further examine the behavior of these functions in the region where potentials do not exist. For the continuous spectrum part we use the functions ψ_k ; when |x| > a they are

$$\psi_k(x) = e^{ikx} + \beta_k e^{-ikx}, \text{ if } kx > 0;$$
 (63a)

$$\psi_k(x) = \gamma_k e^{ikx}, \text{ if } kx < 0.$$
 (63b)

These functions are different from the functions that describe scattering at a potential well in that the sign of the momentum is changed. Functions having such an asymptotic form are convenient because only a term with a single amplitude can satisfy the stationary condition (60) and therefore contribute to the asymptotic expression for the sums in (51), (53) (57). They are one-dimensional versions of the functions having the "incident + convergent wave" asymptotic. The functions ϕ_k are chosen in an analogous fashion.

If α does not equal a singular value, then when $\rho \to \infty$ the arguments of the functions ψ and φ in (51),(53), (57) also increase infinitely. In this case the functions of the discrete spectrum vanish, and (63a), (63b) can be used for the continuous spectrum. Furthermore, using the stationary phase method we get

$$\Psi_1 \sim f(k_1, k_2) \sqrt{\frac{2\pi}{i\kappa\rho}} e^{i\kappa\rho}; \tag{64}$$

$$\Psi_2 \sim g(k_2, k_1) \sqrt{\frac{2\pi}{i \varkappa \rho}} e^{i \varkappa \rho}; \tag{65}$$

$$\Psi_3 \sim \frac{1}{2} h(k, K) \sqrt{\frac{2\pi}{i \varkappa \rho}} e^{i \varkappa \rho},$$
 (66)

where

$$K = k_1 + k_2; \ k = \frac{1}{2} (k_1 - k_2).$$
 (67)

The quantities k_1 and k_2 as functions of α are determined in accordance with (61).

Comparing (62), (64)-(66), we get

$$f(k_1, k_2) = g(k_2, k_1) = \frac{1}{2} h(k, K) = q(k_1, k_2).$$
 (68)

These equalities were obtained when solutions (51),(53),(57) were applied to regions without potentials.*) Thus, (68) can be considered as the condition of joining of the various solutions.

Equalities (68) show that the parts of the continuous spectrum for the functions (51),(53),(57),(58) are not independent. In order to completely define the boundary conditions, it is sufficient to specify only one of them. (Specified, of course, are not the numerical values of the amplitudes, but the general form of the wave function.) In addition, it is necessary to specify the asymptotic corresponding to the excitation of discrete levels for the singular values of α . Since the potential U_{12} does not have bound states, the behavior of the wave function in the direction $\alpha = \frac{\pi}{4}$ is determined if, e.g., (51) is specified; that is, (57) can be constructed if (51) is known. In the usual formulation of the problem the boundary conditions are not imposed for $\alpha = \frac{\pi}{4}$. As is evident, this is also not necessary for a unique determination of the scattering problem.

Note that the shaded area in Figure 1 that corresponds to $\alpha=\frac{\pi}{4}$ makes only an infinitely small contribution to the effective cross sections. To be more precise, when $\rho\to\infty$ the radial flux through this region tends to zero. Generally speaking,

^{*)} A similar relation for the amplitudes <u>f</u> and <u>g</u> was obtained in [9]. The relationship between the amplitudes <u>f</u> and <u>h</u> was determined by Seaton (private communication).

this is not a characteristic of this direction, but a result of the fact that if the streamlines form a divergent beam, the flux at infinity through any line of finite dimensions vanishes. In other words, the zero range of α makes no contribution to the flux. An exception are the directions $\alpha=0$ and $\alpha=\frac{\pi}{2},$ along which a flux corresponding to excitation of discrete levels can be considered as parallel to the axes x_1 or $x_2.$ In these directions the zero range of the angle α makes a finite contribution to the flux. Since the potential in the shaded area corresponding to $\alpha=\frac{\pi}{4}$ is repulsive, the probability and flux densities in this region decrease faster than in the adjacent free-motion regions. This is evident from (57), if the behavior of the functions ϕ_k in the effective region of the repulsive potential is taken into account.*)

$$\Psi_3 \sim \frac{1}{2} h (0, K) \varphi_0 (x_{12}) \sqrt{\frac{2\pi}{iKX}} e^{iKX}$$

where $K = 2\sqrt{E}$. In the region where (63a),(63b) are applicable, this expression is equivalent to (66).

^{*)} Assuming that $X \to \infty$ when $x_{12} = \text{const}$ and applying the stationary phase method to integral (57), we get

Quite a bit of attention is devoted in [14] to the so-called Kato theorems [19]. These theorems define the behavior of the wave function and its derivatives at points where the potential has singularities. Suppose that in our model the potential U_{12} has a certain singularity for $\alpha = \frac{\pi}{4}$. Obviously, all the possible consequences of Kato's theorems for such a case should be manifest in the behavior of the functions $\phi_{\rm K}({\rm x}_{12})$ when ${\rm x}_{12}=0$. It is erroneous to require, as done in [14], that the consequences appear in the asymptotic form that describes motion in a region where the potential is absent.

It should be emphasized that the amplitude \underline{f} for $k_1=k_2$ does not correspond to the case $x_{12}=0$. It corresponds to the following limit process. First, taking a given α , we choose ρ such that $|x_{12}| > a$ and (64) can be applied. Then we make α tend to $\frac{\pi}{4}$. From this it is clear that even in the limit case of $k_1=k_2$ the asymptotic form and the amplitude are associated with large x_{12} and have no relationship with points $x_{12}=0$. The behavior of Υ at $x_{12}=0$ is defined by means of (57) in terms of the behavior of the functions $\phi_k(x_{12})$.

Strictly speaking, the amplitude \underline{f} when $k_1=k_2$ does not have any immediate physical meaning. Regardless of how great the distance to the center is, the interacting electrons cannot move in a row in parallel as free particles. Formula (64) is not applicable for any ρ whatever in the shaded region corresponding

to $\alpha=\frac{\pi}{4}$. As has already been mentioned, the closer α is to $\frac{\pi}{4}$, the greater ρ must be to apply the asymptotic form. If $\alpha=\frac{\pi}{4}$, the domain of application disappears (it has receded to infinity). When $\alpha=\frac{\pi}{4}$ the amplitude has only the meaning of the limit

$$f\left(\frac{\pi}{4}\right) \equiv \lim_{\alpha \to \frac{\pi}{4}} f(\alpha). \tag{69}$$

This fact is not essential, since we should expect limit (69) to equal zero. The behavior of the amplitude $f(k_1, k_2)$ is connected with the behavior of the function $\phi_k(x_{12})$, where $k=\frac{1}{2}$ (k_1-k_2) , describing the relative motion of the two electrons. As we know, when k=0, the coefficient of passage through the barrier equals zero and the wave function within the barrier equals zero.

5. Temkin's Model

The specific analysis of asymptotic behavior given in [14] was carried out on the basis of a model that can be obtained if in the problem of electron collision with a hydrogen atom the real interaction potential $\frac{1}{r_{12}}$ is replaced by the quantity

$$\gamma(r_1, r_2) = r_1^{-1}, \text{ if. } r_1 \ge r_2;$$

$$\gamma(r_1, r_2) = r_2^{-1}, \text{ if } r_1 \le r_2. \tag{70}$$

Then, if the total orbital moment equals zero, the solution to the Schrödinger equation depends only on r_1 and r_2 (or on substituting $1 + r_2 = 1 +$

The quantity $V(\Omega)$ in this model equals

$$V(\alpha) = -\frac{1}{\sin \alpha}, \quad \text{if} \quad \alpha \leq \frac{\pi}{4};$$

$$V(\alpha) = -\frac{1}{\cos \alpha}, \quad \text{if} \quad \alpha \geq \frac{\pi}{4}.$$

$$(71)$$

The potential as a function of α has an inflection point at $\alpha = \frac{\pi}{4}$. The derivative $dV/d\alpha$ at this point becomes discontinuous. This characteristic of the potential leads to some difficulty, and this difficulty was apparently the first reason why asymptotic (28) was criticized in [14].

Since $V(\alpha)$ is finite when $\alpha = \frac{\pi}{4}$, relation (29) is satisfied for a sufficiently large ρ and it can be anticipated that asymptotic (28) is also applicable in this direction. By differentiating the asymptotic form with respect to α , we get

$$\frac{\partial \psi}{\partial \alpha} \sim \rho^{-\frac{5}{2}} \left(\frac{df}{d\alpha} - \frac{i}{\varkappa} \frac{dV}{d\alpha} f \ln \rho \right) e^{i\varkappa \rho - \frac{i}{\varkappa} V \ln \rho} \tag{72}$$

Since $dV/d\alpha$ has a discontinuity when $\alpha = \frac{\pi}{4}$, it follows from (72) that $\partial\psi/\partial\alpha$ also becomes discontinuous in this case. But this is not permissible, since then $\partial^2\psi/\partial\alpha^2$ would have a δ -type singularity. This is not compatible with the fact that all the other terms of the Schrödinger equation are finite.

This difficulty is absent in the triplet case, since then, because of antisymmetry with respect to r_1 and r_2 , the wave function ψ and the amplitude \underline{f} equal zero when $\alpha = \frac{\pi}{4}$ (let us remember that $\alpha = \frac{\pi}{4}$ corresponds to $r_1 = r_2$). In the singlet (symmetrical) case, however, the amplitude may be different from zero. In this case the wave function and amplitude satisfy the conditions

$$\frac{\partial \psi}{\partial \alpha} = \frac{df}{d\alpha} = 0, \quad , \quad \text{if} \quad \alpha = \frac{\pi}{4}. \tag{73}$$

Obviously, (73) is not compatible with (72) if $f(\frac{\pi}{h}) \neq 0$.

In the preceding section of this article the remark was made that the amplitude of the joint motion of repulsive particles should equal zero. The model being considered here refers to a three-dimensional space. If $\alpha = \frac{\pi}{4}$, then the absolute magnitudes of the velocities are equal, while their directions may be different, for example, opposite. There is no reason to assume that the amplitude for all the different directions equals zero.

To solve the difficulty that has arisen, note that at great distances it should be possible to apply the quasi-classical approximation, in which

$$\Psi(\rho,\alpha) \sim \rho^{-\frac{5}{2}} f(\alpha) e^{iS(\rho,\alpha)}$$
 (74)

where S is the action integral of classical mechanics. In the last section of this article it was shown that in the symmetrical case, with $\alpha = \frac{\pi}{4}$, the derivative of the asymptotic form of the action integral does not equal the asymptotic form of the derivative of this function; that is, the asymptotic form cannot be differentiated. According to (74), the same is true of the wave function. When $\alpha = \frac{\pi}{4}$, formula (72) is not applicable. If $\alpha \rightarrow \frac{\pi}{4}$, the domain of application of (72) recedes to infinity. In the model being analyzed, (28) is applicable when $\alpha = \frac{\pi}{4}$, but it cannot be said that expansion (27) is also applicable, since infinite differentiability of the function $V(\Omega)$ is required for its derivation.

Another explanation for the above-outlined difficulty was given in [14], namely, that asymptotic form (28) is not correct (not for any value of α). Proposed as the asymptotic form instead of (28) was a superposition of the products of the s-components of a plane wave and a Coulomb function

$$\frac{1}{r_1 r_2} \int_0^{\kappa} C(k_2) e^{ik_1 r_1} F_{k_2}(r_2) dk_2, \tag{75}$$

which is obtained if the rapidly decreasing terms are omitted in the solution of the so-called zeroth-order problem. In (75) the F are Coulomb radial functions having the asymptotic

$$F \sim \sin\left[kr + \frac{1}{k} \ln 2kr + \arg\Gamma\left(1 - \frac{i}{k}\right)\right]. \tag{76}$$

It is not difficult to see that (75) is the analog of (18). Substituting (76) into (75), we get the asymptotic form (28) by means of the stationary-phase method*, which is the same way as (20) was derived. Thus the results of [14] confirm the same asymptotic form that is denied in this article. They indicate that no other asymptotic exists, despite the assertion of the author of [14].

Note also that (75) was transformed in fact to (28) (more precisely to (20)) in [3]. According to (71), for the potential energy of the system we have

$$\frac{V(\alpha)}{\rho} = -\frac{1}{r_2}, \quad \text{if } r_1 \ge r_2;$$

$$\frac{V(\alpha)}{\rho} = -\frac{1}{r_1}, \quad \text{if } r_1 \le r_2.$$

$$(77)$$

^{*}In [14] the applicability of the stationary-phase method to superposition (75) is denied. In his next paper [20], however, the author of [14] refrains from objecting to the applicability of the stationary-phase method and admits that (28) and (75) are equivalent. But he finds the solution of the above-described difficulty to lie in the fact that the singlet amplitude should also equal zero when $\alpha = \frac{\pi}{4}.$

It is evident that the Coulomb potential acts on only one of the electrons. Therefore, the model being considered relates to the case of a single neutral particle and two charged particles, as investigated in [3].

An asymptotic form for the exact collision problem was also proposed in [14]. It has the form of a cumbersome series for which the necessary condition of the asymptotic form is not fulfilled, i.e., the series does not identically satisfy the Schrödinger equation with accuracy up to second-order terms.

6. Real Particles

The basic characteristics of the one-dimensional model we have examined are also valid for real Coulomb interaction particles in three-dimensional space.

In this case the potential $V(\Omega)$ tends to infinity in the singular directions. If Ω approaches a singular value, the domain of applicability of (28) goes to infinity.

In the case of short-range forces, asymptotic form (1) does not in itself contain singularities in singular-valued angles Ω (the exponent imp does not depend on the angles). Therefore, if a careless approach is used, it may turn out that (1) is applicable for the singular directions also. But from all that has been outlined above, it is clear that this is not so. Asymptotic form (1) signifies the approximation of plane waves

and is applicable only where the potential energy need not be taken into account.

Analogously, asymptotic form (28) for charged particles is applicable only where the Coulomb potential energy is low as compared with the kinetic energy. In such a case the asymptotic form depends explicitly on Ω . If it is applied in singular directions, a meaningless expression is obtained. Obviously it is incorrect to conclude from this fact, as was done in [14], that asymptotic form (28) cannot be used anywhere.

It should be emphasized that the singularity in the asymptotic form is in no way related, generally speaking, to the singularity in the Coulomb potential for $r_{12}=0$. The asymptotic form is governed by the behavior of the potential at great distances. If the Coulomb potential at short distances is replaced by a potential that is finite at zero, nothing is changed in the asymptotic form.

The ionization amplitude at ${\bf k}_1={\bf k}_2$ corresponds to a passage to the limit in which Ω approaches a singular value, but for every Ω there is found a value of ρ at which r_{12} is very large. Hence it is clear that both the scattering amplitude and the asymptotic form always refer to $r_{12}\sim \infty$ and have no relationship to $r_{12}=0$. Consequently, the Kato theorems cannot be applied to them, since they relate to the region where $r_{12}=0$.

An expression analogous to (57), describing the behavior of the wave function for r_{12} = 0, can also be formulated in the case of real particles. All the characteristics implied by Kato's theorems and Coulomb repulsion should be found in the Coulomb functions $\varphi_k(r_{12})$.

Note that the Coulomb repulsion functions decay exponentially for every given distance if the momentum tends to zero. On this basis it can be anticipated that the scattering amplitude will vanish as $k_1 \rightarrow k_2$.

This is evident from the integral expressions. According to [10,13],

$$f(\mathbf{k}_1, \mathbf{k}_2) \sim \langle \Psi \mid H - E \mid \Phi \rangle,$$
 (78)

where Ψ is the exact wave function, while Φ is a certain function, regular at zero, which has the same asymptotic as the exact wave function, in a direction corresponding to the given amplitude; that is, it satisfies conditions (35),(36).

When $k_1 \approx k_2$, it is convenient to choose Φ in a form equivalent to (57). Such a form is

$$\Phi = \varphi (\alpha_1, k, r) \varphi (\alpha_2, K, R), \tag{79}$$

where

$$k = \frac{1}{2}(k_1 - k_2); r = r_1 - r_2;$$
 (80)

$$K = k_1 + k_2; R = \frac{1}{2}(r_1 + r_2);$$
 (81)

$$\alpha_1 = \frac{1}{|\mathbf{k}_1 - \mathbf{k}_2|} = \frac{1}{2k}; \tag{82}$$

$$\alpha_2 = -\frac{1}{k_1} - \frac{1}{k_2} = -\frac{4\zeta}{K}. \tag{83}$$

The Coulomb functions ϕ are determined in accordance with (14).

The function Φ describes the relative motion of the two electrons and the motion of their center of inertia. The latter is assumed to be moving in a field set up by the effective charge ζ , which is determined by (83).

Due to the exponential decrease of the wave function of relative motion as $k \rightarrow 0$, it can be expected that the amplitude will vanish as $k_1 \rightarrow k_2$. Physically it is completely clear that the amplitude of joint motion of the repulsive particles equals zero.

7. Asymptotic Behavior in Classical Mechanics

In order to get a clearer picture of asymptotic behavior, it is useful to consider this problem from the viewpoint of

classical mechanics. Moreover, as is well known, in the range of large distances, where a quasi-classical approximation can be used, the classical solution of the equations of motion corresponds directly to the quantum solution.

Let us briefly consider an example of the problem of electron ionization of a hydrogen atom at a total orbital moment of zero.

In this case the motion is defined by three coordinates:

$$\rho = \sqrt{r_1^2 + r_2^2}; \ \alpha = \arctan \left(\frac{r_2}{r_1}; \ \Theta = \angle (r_1, r_2). \right)$$
 (84)

For the Hamiltonian we have

$$H = T_{\rho} + \rho^{-2} T^* + \rho^{-1} V(\alpha, \Theta), \tag{85}$$

where

$$T_{\rho} = \frac{1}{2} P_{\rho}^{2}; \qquad (86)$$

$$T^* = \frac{1}{2} \left(p_{\alpha}^2 + \frac{4}{\sin^2 2\alpha} p_0^2 \right); \tag{87}$$

$$V(\alpha, \Theta) = -\frac{1}{\sin \alpha} - \frac{1}{\cos \alpha} + \frac{1}{\sqrt{1 - \sin 2\alpha \cos \Theta}}.$$
 (88)

The canonic equations have the following form:

$$\dot{\mathfrak{p}} = p_{\mathfrak{p}}; \tag{89}$$

$$\dot{\alpha} = \frac{1}{\rho^2} p_{\alpha}; \qquad (90)$$

$$\dot{\Theta} = \frac{4}{\rho^2 \sin^2 2\alpha} p_{\Theta}; \tag{91}$$

$$\dot{p}_{\rho} = \frac{1}{\rho^3} \left(p_{\alpha}^2 + \frac{4}{\sin^2 2\alpha} p_{\theta}^2 \right) + \frac{V}{\rho^2} ; \tag{92}$$

$$\dot{p}_{\alpha} = \frac{8\cos 2\alpha}{\rho^2 \sin^3 2\alpha} p_{\Theta}^2 - \frac{1}{\rho} \frac{\partial V}{\partial \alpha}; \tag{93}$$

$$\dot{p}_{\Theta} = -\frac{1}{\rho} \frac{\partial V}{\partial \alpha}. \tag{94}$$

The dot above a symbol denotes a time-derivative.

Before solving system (89-94), let us investigate the case of free motion. In this case

$$\mathbf{r}_i = \mathbf{v}_i \ t + \mathbf{c}_i, \tag{95}$$

where \mathbf{v}_{i} and \mathbf{c}_{i} are constants.

We substitute (95) into (84). Taking (89)-(91) into account, we get, as $t\rightarrow\infty$,

$$\rho = \varkappa t + O(1); \tag{96}$$

$$\alpha = \text{const} + O(t^{-1}); \tag{97}$$

$$\Theta = \text{const} + O(t^{-1}); \tag{98}$$

$$p_{\rho} = \varkappa + O(t^{-2}); \tag{99}$$

$$p_{\alpha} = \text{const} + O(t^{-2}); \tag{100}$$

$$p_{\Theta} = \text{const} + O(t^{-2}). \tag{101}$$

For the kinetic energy components we obtain

$$T_{\rho} \sim \frac{\kappa^2}{2}; \ \rho^{-2} T^* \sim \rho^{-2} \text{ const.}$$
 (102)

The fact that the angular part of the kinetic energy is somewhat smaller than the radial part at great distances has a distinct physical, or rather metrical meaning. It expresses the fact that at great distances motion actually takes place in a radial direction. In other words, the particle source (reaction zone) can be considered as a point located at the origin. Note that the vectors $\mathbf{c}_{\mathbf{i}}$ characterize divergence of the source from the origin. If $\mathbf{c}_{\mathbf{i}} = \mathbf{0}$, then $\mathbf{T}^* = \mathbf{0}$ for all values of $\underline{\mathbf{t}}$.

Let us return to equations (89)-(94). In the presence of Coulomb forces motion cannot be considered completely free even at great distances. However, if the concept of scattering is

at all applicable in this case, then at great distances the trajectories should approach the free-motion trajectories asymptotically, and this is expressed by the boundary conditions:

$$\rho \to \kappa t; \ \alpha \to \text{const}; \ \Theta \to \text{const} \ (t \to \infty).$$
 (103)

The boundary conditions determine the first term in the asymptotic expansion. In order to find the next term, we substitute the expressions (96)-(101), which correspond to free motion, into the right sides of equations (89)-(94). Then we find that in determining the first terms of the asymptotic solution we can neglect the kinetic-energy terms on the right-hand side, and the quantity $V(\alpha, \theta)$ and its derivatives can be considered as constants. After integration we get

$$\rho = \varkappa t - \frac{V}{\varkappa^2} \ln t + O(1); \qquad (104)$$

$$\alpha = \text{const} + O(t^{-1} \ln t); \tag{105}$$

$$\Theta = const + O(t^{-1} \ln t); \tag{106}$$

$$p_{p} = \varkappa - \frac{V}{\varkappa^{2}t} + O(t^{-2}); \tag{107}$$

$$p_{\alpha} = -\frac{1}{\varkappa} \cdot \frac{\partial V}{\partial \alpha} \ln t + O(1); \qquad (108)$$

$$p_{\Theta} = -\frac{1}{\varkappa} \cdot \frac{\partial V}{\partial \Theta} \ln t + O(1). \tag{109}$$

In these expressions the angular momenta p_{α}, p_{θ} are observed to differ most from the free-motion formulas (96)-(101); now they diverge logarithmically as $t\rightarrow\infty$. However, if (104)-(109) are substituted into the right-hand sides of equations (89)-(94), these differences prove to be insignificant, and after integration we again get (104)-(109); that is, solution (104)-(109) is self-consistent. Thus, formulas (104)-(109) determine the asymptotic behavior of the exact solution of system (89)-(94).

In the coordinates r_i the classical equations of motion for a system of charged particles have the form

$$\frac{d^2\mathbf{r}_i}{dt^2} = Z_i \sum_{i \neq j} \frac{Z_j (\mathbf{r}_i - \mathbf{r}_j)}{\|\mathbf{r}_i - \mathbf{r}_j\|^3}.$$

The asymptotic solution of this system is

$$\mathbf{r}_i \sim \mathbf{v}_i t - Z_i \sum_{j \neq i} \frac{Z_j (\mathbf{v}_i - \mathbf{v}_j)}{\|\mathbf{v}_i - \mathbf{v}_j\|^3} \ln t.$$

Substitution of this expression into (84) leads to (104)-(109).

For the kinetic-energy components in this case we get

$$T_{\rho} \sim \frac{\kappa^2}{2}, \ \rho^{-2} T^* \sim \rho^{-2} (\ln \rho)^2 \text{ const.}$$
 (110)

As is evident, in the presence of Coulomb interaction the term containing T^* can also be neglected at great distances. This corresponds to the fact that the term containing Δ^* can be neglected in the Schrödinger equation when deriving asymptotic form (28).

Now let us determine the asymptotic behavior in a shorter range. We use the Lagrange form

$$S = 2 \int (T_{\rho} + \rho^{-2} T^{*}) dt. \tag{111}$$

From (110) it is clear that only T_{ρ} should be taken into account. With due regard to (86),(104),(107) we get the already-known result:

$$S \sim \int p_{\rho} d\rho \sim \kappa_{\rho} - \frac{V}{\kappa} \ln \rho.$$
 (112)

The same result is reached by direct solution of the Hamilton-Jacobi equation. This equation can be written in the form

$$T_{\rho} + \frac{T^*}{\rho^2} + \frac{V}{\rho} = E,$$

assuming that in the expressions for T_{ρ} and T^* , namely, (86),(87), the generalized momenta have been replaced by partial derivatives of the action integral:

$$p_{\rho} = \frac{\partial S}{\partial \rho}$$
; $p_{\alpha} = \frac{\partial S}{\partial \alpha}$; $p_{\Theta} = \frac{\partial S}{\partial \Theta}$.

In the first approximation we neglect the term containing T^* . Then we have

$$T_{\rho} \sim E - \frac{V}{\rho}$$
; $\frac{\partial S}{\partial \rho} \sim \sqrt{\kappa^2 - \frac{2V}{\rho}}$,

from which follows (112).

Differentiating (112) we find

$$\frac{\partial S}{\partial x} \sim -\frac{1}{\kappa} \frac{\partial V}{\partial \alpha} \ln \rho$$
, $\frac{\partial S}{\partial \theta} \sim -\frac{1}{\kappa} \frac{\partial V}{\partial \theta} \ln \rho$,

which corresponds to (108),(109). Substituting these expressions into the Hamilton-Jacobi equation, we see that the term $\rho^{-2}T^*$ need not actually be taken into account. Thus, (112) is a self-consistent asymptotic solution of the Hamilton-Jacobi equation.

In addition, let us consider Temkin's model from the viewpoint of classical mechanics. In this case exact solutions to equations (89)-(94) can be found.

Instead of (88) let us take expression (71) for the quantity V. It does not depend on the angle θ , and therefore we can set

$$\theta = \text{const} \text{ and } p_{\theta} = 0.$$
 (113)

It remains to determine ρ and α as functions of time. Instead of using them for the given problem, it is more convenient to use the coordinates r_1 and r_2 . Let us consider the region where $r_1 \geq r_2$. The equations of motion, according to (77), have the form

$$\frac{d^2r_1}{dt^2} = 0; \quad \frac{d^2r_2}{dt^2} = -\frac{1}{r_2^2} \quad (r_1 \geqslant r_2). \tag{114}$$

Equations (114) describe free motion of the first electron and Coulomb motion of the second and are solved in terms of elementary functions:

$$r_1 = C_1 + v_1 t; (115)$$

$$C_2 + u_2 t = \frac{v_2}{u_2} r_2 - \frac{1}{u_2^2} \ln \frac{v_2 + u_2}{v_2 - u_2}, \tag{116}$$

where C_1 , C_2 , and v_1 are constants;

$$v_2^2 = u_2^2 + \frac{2}{r_2}; \ u_2^2 = \varkappa^2 - v_1^2; \ \varkappa^2 = 2E.$$
 (117)

It is obvious that u_2 is the velocity of the second electron at infinity.

Omitting \underline{t} from (115),(116), we get the equation for the trajectory in coodinate space:

$$C + r_1 = \frac{v_1 v_2}{u_2^2} r_2 - \frac{v_1}{u_2^3} \ln \frac{v_2 + u_2}{v_2 - u_2}.$$
 (118)

For a given total energy of the system, E, equation (118) contains two arbitrary parameters C and v_1 ; that is, it determines a two-parameter family of trajectories.

Note that if (117) is taken into account, the argument of the logarithm in (116) can be written in the form

$$\frac{v_2 + u_2}{v_2 - u_2} = (v_2 u_2 + u_2^2) r_2 + 1. \tag{119}$$

When $t\rightarrow \infty$, equations (115), (116), and (118) take the form

$$r_1 \sim v_1 t;$$
 (120)

$$r_2 \sim v_2 t + \frac{1}{v_2^2} \ln 2v_2^3 t;$$
 (121)

$$\frac{r_1}{v_1} \sim \frac{r_2}{v_2} - \frac{1}{v_2^3} \ln 2 \, v_2^2 \, r_2. \tag{122}$$

Hence, for ρ and α we get expressions (104),(105), where V is determined in accordance with (71).

Furthermore, let us consider trajectories corresponding to the symmetric case of quantum mechanics.

The symmetric wave function satisfies the condition

$$\frac{\partial \Psi}{\partial \alpha} = 0$$
, if $\alpha = \frac{\pi}{4}$. (125)

This means that when $\alpha=\frac{\pi}{\mu}$ (that is, when $r_1=r_2$), the flux has a radial direction. Consequently, the corresponding classical trajectories satisfy the equation

$$v_1 = v_2$$
, if $r_1 = r_2$. (124)

Taking (117) into account, for $r_1 = r_2 = r$ and $v_1 = v_2 = v$ we have

$$v = \sqrt{E + \frac{1}{r}}; \quad r = \frac{1}{v^2 - E}.$$
 (125)

Comparing (118), (124), (125), we get

$$C = \frac{2}{u_2^2} - \frac{v_1}{u_2^3} \ln \frac{v_1 + u_2}{v_1 - u_2}.$$
 (126)

Thus, trajectories corresponding to the symmetric case of quantum mechanics form a one-parameter family at a given E.

In connection with the problem that arises when Temkin's model is examined from a quantum-mechanical viewpoint, let us study the asymptotic behavior in a shorter range.

The Hamilton-Jacobi equation has the form

$$\left(\frac{\partial S}{\partial r_1}\right)^2 + \left(\frac{\partial S}{\partial r_2^2}\right)^2 - \frac{1}{r_2} = E. \tag{127}$$

The complete integral of this equation is

$$S = \int v_1 dr_1 + \int v_2 dr_2 = \omega + Y(r_1, r_1, r_2), \qquad (128)$$

where

$$Y = v_1 r_1 + v_2 r_2 + \frac{1}{u_2} \ln \frac{v_2 + u_2}{v_2 - u_2};$$
 (129)

 $\mbox{\ensuremath{\textbf{w}}}$ and $\mbox{\ensuremath{\textbf{v}}}_1$ are arbitrary constants; $\mbox{\ensuremath{\textbf{v}}}_2$ and $\mbox{\ensuremath{\textbf{u}}}_2$ are determined by (117).

In the symmetric case we have the condition

$$\frac{\partial S}{\partial \alpha} = 0$$
, if $\alpha = \frac{\pi}{4}$. (130)

considering that

$$\frac{\partial S}{\partial r_1} = v_1; \quad \frac{\partial S}{\partial r_2} = v_2, \tag{131}$$

$$\frac{\partial}{\partial \alpha} = \rho \left(-\sin \alpha \, \frac{\partial}{\partial r_1} + \cos \alpha \, \frac{\partial}{\partial r_2} \right),\tag{132}$$

we can see that (130) is equivalent to (124).

Condition (130) can be satisfied by a particular value of the total integral of equation (127). The total integral can be obtained by considering ω as a function of v_1 , and v_1 as a

function of r_1 and r_2 , defined by the condition

$$\frac{d\omega}{dv_1} + \frac{\partial Y}{\partial v_1} = 0. \tag{133}$$

By substituting (129) into (133) we get

$$\frac{d\omega}{dv_1} = C(v_1, r_1, r_2), \tag{134}$$

where C is determined by (118).

We must find a function $\,\omega(v_1)\,$ such that it ensures the fulfillment of (130).

Setting $r_1 = r_2$ in (134) and taking (125) into account, we find

$$\frac{d\omega}{dv_1} = C(v_1),\tag{135}$$

where C as a function of v_1 is determined by (126).

Hence

$$\omega = \int C(v_1) dv_1 = \frac{1}{\sqrt{E}} \ln \frac{v_1 + \sqrt{E}}{2(v_1 - \sqrt{E})} - \frac{1}{u_2} \ln \frac{v_1 + u_2}{v_1 - u_2}.$$
 (136)

The integration constant is chosen such that

$$\omega = 0$$
, if $v_1 = u_2 = \sqrt{E}$. (137)

Note that according to (125),

$$v_1 \rightarrow \sqrt{E}$$
, if $r_1 = r_2 \rightarrow \infty$. (138)

The equation determining $\nu_{\rm l}$ as a function of $r_{\rm l}$ and $r_{\rm 2}$ is obtained by comparing (134) and (135). It has the form

$$2 - \frac{v_1}{u_2} \ln \frac{v_1 + u_2}{v_1 - u_2} = -u_2^2 r_1 + v_1 v_2 r_2 - \frac{v_1}{u_2} \ln \frac{v_2 + u_2}{v_2 - u_2}.$$
 (139)

The asymptotic solution of this equation in the coordinates ρ and α for $\rho \longrightarrow \infty$ and $\alpha \neq \frac{\pi}{.4}$ has the form

$$v_1 \sim \varkappa \cos \alpha + \frac{\operatorname{ctg} \alpha}{\varkappa} \cdot \frac{\ln \beta}{\rho};$$
 (140)

$$v_2 \sim \alpha \sin \alpha - \frac{\operatorname{ctg}^2 \alpha}{\alpha} \cdot \frac{\ln \rho}{\rho}$$
 (141)

These solutions were obtained under the condition that in the asymptotic region the logarithm on the right-hand side of (139) is considerably greater than that on the left-hand side, and this condition is fulfilled for a sufficiently large ρ , if $\alpha \neq \frac{\pi}{4}$ (to which $v_1 \neq u_2$ corresponds). If $\alpha \rightarrow \frac{\pi}{4}$, then $v_1 \rightarrow u_2$ and an even greater ρ is necessary for the given proposition to be valid. In other words, if $\alpha \rightarrow \frac{\pi}{4}$, the domain of applicability of (140), (141) goes to infinity. When $\alpha = \frac{\pi}{4}$, the logarithmic terms on both sides of (139) are equal and (139) reduces to (124), (125). Instead of (140), (141) we can then write

$$v_1 \sim \alpha \cos \alpha + \frac{1}{\alpha p}; \qquad (142)$$

$$v_2 \sim \varkappa \sin \alpha + \frac{1}{\varkappa \rho} \,. \tag{143}$$

The difference between (140), (141) and (142), (143) is not essential when determining the asymptotic behavior of the action. Substituting (140), (141) or (142), (143) into (128), (129), we get in both cases

$$S \sim Y \sim \kappa \rho + \frac{1}{\kappa \sin \alpha} \ln \rho,$$
 (144)

which, when (71) is taken into account, is equivalent to (30).

The situation is somewhat different when studying the asymptotic behavior of the derivative $\partial S/\partial \alpha$.

Taking (131), (132) into account

$$\frac{\partial S}{\partial \alpha} = \rho \left(-v_1 \sin \alpha + v_2 \cos \alpha \right). \tag{145}$$

Substitution of (140), (141) into (145) leads to

$$\frac{\partial S}{\partial \alpha} \sim \frac{\partial Y}{\partial \alpha} \sim -\frac{\cos \alpha}{\alpha \sin^2 \alpha} \ln \rho,$$
 (146)

whereas (142), (143) lead to (130).

Expression (146) can also be gotten by differentiating asymptotic form (144) with respect to α . Thus, when $\alpha=\frac{\pi}{4}$, the derivative of the asymptotic form does not equal the asymptotic form of the derivative.

The reason why (144) is applicable when $\alpha = \frac{\pi}{4}$, while (146) is not, is that $\omega(v_1)$ is bounded in the neighborhood of $v_1 = \sqrt{E}$, while the derivative $d\omega/dv_1$ diverges logarithmically. Formula (146) is applicable in the region where $d\omega/dv_1$ need not be accounted for; as $\alpha \to \frac{\pi}{4}$, this region tends to infinity.

The asymptotic expressions we have obtained are not applicable when $\alpha=0$, because the function $V(\alpha)$, determined by (71), has a pole when $\alpha=0$.

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Translated by

A. Schidlovsky

Revised by

Dr. Andre L. Brichant

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